Acta Cryst. (1975). B31, 1242

The Structure of the Rubidium Salt of *N*-(Purin-6-ylcarbamoyl)-L-threonine Tetrahydrate, a Hypermodified Base in the Anticodon Loop of Some tRNA's

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(*Received* 2 *November* 1974; *accepted* 6 *December* 1974)

$C_{10}H_{11}N_6O_4Rb\ 4H_2O$ is monoclinic, space group $P2_1$, with $a=8{\cdot}901$ (3), $b=6{\cdot}455$ (2), $c=15{\cdot}379$ (5) Å, $\beta=105{\cdot}43$ (4)°, $Z=2$. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations to a final R of 0·050 for 1190 counter reflexions. The molecules exist in the N(9)–H tautomeric form. The molecular geometry is determined by the conformationally preferred internal hydrogen bond between N(12)–H of the ureidothreonine side chain and N(1) of purine, 2·693 Å. The purine rings display approximately parallel, head-to-tail stacking with an interplanar spacing of about 3·2 Å. Rb is coordinated by one N and five O atoms. The water molecules form two hydrophilic zones in the crystal.

Introduction

The hypermodified nucleoside *N*-[9-(β-D-ribofuranosyl) purin-6-ylcarbamoyl]-L-threonine is found in several tRNA's (Chheda *et al.*, 1969; Miller & Schweizer, 1972). It is located at a position adjacent to the 3'-ends of the anticodon triplets of tRNA that respond to codons beginning with adenosine (Ishikura, Yamada, Murao, Saneyoshi & Nishimura, 1969; Powers & Peterkofsky, 1972). The presence of this hydrophilic residue in tRNA may be essential for the conformation of the anticodon loop and the formation of an anticodon-messenger-ribosome complex. More is known about hydrophobic residues which can occur at the same position (Hall, 1971; Bugg & Thewalt, 1972; McMullan & Sundaralingam, 1971) and which prevent hydrogen bonding at the purine N(1) site. To investigate the influence of hydrophilic side chains we are studying the molecular structure of *N*-(purin-6-ylcarbamoyl)-L-threonine tetrahydrate.

In this paper we report the determination of the structure of the Rb salt of *N*-(purin-6-ylcarbamoyl)-L-threonine tetrahydrate.

During our studies, Parthasarathy, Ohrt & Chheda (1973) have given preliminary results of their work on the K salt of *N*-(purin-6-ylcarbamoyl)-L-threonine and related compounds. More recently Parthasarathy, Ohrt & Chheda (1974) published the crystal structure of the K salt of *N*-(purin-6-ylcarbamoyl)glycine monohydrate.

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Experimental

The compound was synthesized by the urethane method (Chheda & Hong, 1971) and crystallized from an ethanol–ethyl acetate mixture by Dr R. W. Adamiak, Institute of Organic Chemistry of the Polish Academy of Sciences. The space group was determined from precession and Weissenberg photographs. The systematic absence of $0k0$ with k odd suggests that the space group is either $P2_1$ or $P2_1/m$. The former was adopted since the compound is optically active and was confirmed by the structure analysis. Cell dimensions were obtained from calibrated zero-layer Weissenberg photographs and refined on a Hilger–Watts four-circle diffractometer.

Crystal data

$C_{10}H_{11}N_6O_4Rb.4H_2O$. Monoclinic, space group $P2_1$. $a=8{\cdot}901$ (3), $b=6{\cdot}455$ (2), $c=15{\cdot}379$ (5) Å, $\beta=105{\cdot}43$ (4)°; $V=851{\cdot}77$ Å^3; $Z=2$; D_x† $=1{\cdot}70$ g cm^{-3}; μ(Cu $K\alpha$) $=49{\cdot}16$ cm^{-1}.

The crystal (0·03 × 0·70 × 0·02 mm) was mounted along **b**. 1190 independent reflexions were collected on a Hilger–Watts four-circle diffractometer with Cu $K\alpha$ radiation for θ between 0 and 55°. An ω, θ scan of 40 steps of 0·02° for $\theta<25°$ and of 50 steps for $25°<\theta<55°$ was employed with the ordinate analysis technique (Watson, Shotton, Cox & Muirhead, 1970). The step time was 1s for $\theta<25°$ and 1·5s for $25°<\theta<55°$.

† A value for the experimental density was not obtained owing to the lack of suitable crystals.

The intensities of three standard reflexions were monitored every 50 reflexions. Lorentz and polarization corrections were made. An absorption correction was applied (North, Phillips & Matthews, 1968). Data were collected over one hemisphere and four equivalent reflexions were merged. The merging R [$= \sum_h \sum_i (I_{hi} - \bar{I}_h) / \sum_h \sum_i I_{hi}$] was 0·04.

Structure determination and refinement

The Rb position was determined from a Patterson map. The resulting electron density map ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$ was 0·337) contained two superposed, mirror-plane-related images of the molecule, but indicated the position of the atoms of the planar purine ring. The addition of these atoms to the model removed the false symmetry and from the new electron density map ($R = 0{\cdot}248$) all the non-hydrogen atoms were located (except in H_2O) ($R = 0{\cdot}167$). The further inclusion of the O atoms of four H_2O molecules and a full-matrix least-squares refinement with individual isotropic temperature factors led to an R of 0·092. Refinement was continued with anisotropic thermal parameters for Rb, giving $R = 0{\cdot}067$. The positions of seven H atoms were calculated geometrically (C–H = 1·05 Å, N–H = 0·95 Å) and compared with a difference synthesis. Agreement was good in all cases. The isotropic thermal parameters of the H atoms were refined. After the last cycle of full-matrix least-squares calculations with anisotropic thermal parameters for all non-hydrogen atoms, R was 0·050.* Scattering factors and anomalous dispersion corrections for Rb were taken from *International Tables for X-ray Crystallography* (1968). The X-RAY 70 System (Stewart, Kundell & Baldwin, 1970) was used for the calculations.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30807 (6pp). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

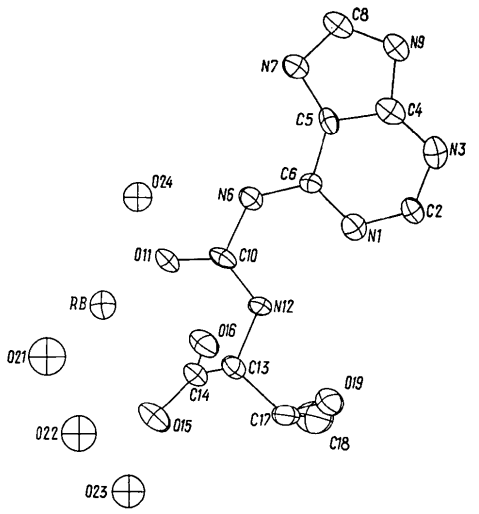

Fig. 1. Thermal ellipsoids of the non-hydrogen atoms (enclosing 50% probability).

Table 1. *Fractional atomic coordinates with standard deviations in parentheses* ($\times 10^4$) *and isotropic thermal parameters for the oxygen atoms of the water molecules and for the hydrogen atoms*

	x	y	z	U_{iso}
Rb	−32 (1)	7500	7206 (1)	
N(1)	5654 (10)	1175 (15)	6053 (6)	
C(2)	6998 (12)	1155 (17)	5812 (7)	
N(3)	7163 (10)	1007 (15)	4961 (6)	
C(4)	5769 (13)	984 (17)	4348 (7)	
C(5)	4311 (11)	1058 (18)	4500 (7)	
C(6)	4295 (11)	1098 (17)	5420 (6)	
N(7)	3115 (10)	980 (16)	3702 (6)	
C(8)	3899 (14)	844 (19)	3092 (7)	
N(9)	5476 (10)	850 (14)	3414 (6)	
N(6)	2911 (10)	1034 (16)	5643 (6)	
C(10)	2626 (12)	1131 (18)	6518 (6)	
O(11)	1266 (8)	1061 (14)	6555 (4)	
N(12)	3868 (9)	1310 (17)	7217 (5)	
C(13)	3630 (13)	1505 (22)	8111 (7)	
C(14)	2748 (13)	3494 (20)	8225 (7)	
O(15)	2015 (9)	3341 (14)	8848 (5)	
O(16)	2748 (9)	5054 (14)	7764 (5)	
C(17)	5211 (14)	1404 (23)	8826 (7)	
C(18)	5950 (18)	−776 (26)	8858 (10)	
O(19)	6213 (9)	2933 (17)	8626 (5)	
O(21)	−1069 (12)	1559 (19)	7960 (7)	70 (3)
O(22)	248 (10)	6575 (16)	9095 (6)	58 (2)
O(23)	1878 (10)	9979 (15)	9941 (5)	49 (2)
O(24)	95 (8)	5109 (14)	5627 (5)	41 (2)
H(2)	8026	1233	6340	44
H(6)	2007	895	5152	44
H(8)	3337	709	2402	44
H(9)	6214	782	3068	44
H(12)	4848	1247	7264	44
H(13)	2963	208	8185	44
H(17)	5045	1750	9461	44

Table 2. *Atomic thermal parameters with standard deviations in parentheses* (Å$^2 \times 10^3$, *except* Å$^2 \times 10^4$ *for* Rb)

The temperature factor has the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rb	336 (6)	464 (7)	387 (6)	−15 (7)	108 (4)	−10 (7)
N(1)	34 (5)	26 (6)	35 (5)	−5 (4)	14 (4)	−4 (4)
C(2)	30 (6)	24 (7)	34 (6)	−2 (5)	16 (5)	−1 (5)
N(3)	32 (5)	23 (5)	49 (6)	−4 (4)	16 (5)	−4 (4)
C(4)	48 (7)	11 (6)	33 (6)	−5 (5)	19 (5)	−7 (5)
C(5)	24 (5)	24 (7)	37 (6)	2 (5)	19 (5)	7 (5)
C(6)	26 (6)	30 (7)	19 (5)	−1 (5)	7 (4)	−3 (5)
N(7)	37 (5)	40 (6)	28 (5)	1 (5)	13 (4)	−2 (5)
C(8)	48 (7)	34 (7)	34 (6)	−1 (6)	22 (5)	1 (5)
N(9)	36 (5)	24 (5)	35 (5)	0 (4)	20 (4)	0 (4)
N(6)	30 (5)	35 (6)	26 (4)	3 (4)	11 (4)	0 (4)
C(10)	42 (7)	29 (7)	22 (5)	6 (5)	19 (5)	0 (5)
O(11)	32 (4)	56 (6)	27 (4)	2 (4)	19 (3)	0 (4)
N(12)	27 (5)	47 (6)	16 (4)	5 (5)	9 (4)	−6 (4)
C(13)	31 (6)	46 (7)	28 (6)	2 (6)	15 (5)	8 (5)
C(14)	30 (6)	41 (7)	25 (6)	2 (6)	14 (5)	−1 (6)
O(15)	57 (5)	45 (6)	40 (4)	3 (4)	32 (4)	0 (4)
O(16)	49 (5)	41 (5)	37 (4)	9 (4)	23 (4)	10 (4)
C(17)	45 (7)	57 (8)	19 (5)	13 (7)	9 (5)	2 (6)
C(18)	71 (10)	64 (11)	57 (8)	31 (9)	18 (7)	7 (8)
O(19)	45 (5)	59 (8)	40 (4)	−11 (5)	16 (4)	0 (5)

Table 3. *Devations* (Å) *of the atoms from the least-squares planes through the purine ring* (*plane* 1) *and through the chain* (*plane* 2)

	Plane 1		Plane 2
N(1)	−0·007	N(6)	−0·001
C(2)	0·018	C(10)	−0·009
N(3)	−0·008	O(11)	−0·037
C(4)	0·006	N(12)	0·030
C(5)	0·021	C(13)	0·083
C(6)	−0·026	C(17)	−0·066
N(7)	0·017		
C(8)	−0·012		
N(9)	−0·011		

Table 4. *Comparison of the bond distances and angles in the adenine moiety of the* Rb *salt of N-(purin-6-yl-carbamoyl)-*L*-threonine tetrahydrate* (*R*) *with the value in the average unprotonated* (*U*) *and protonated* (*P*) *adenine compounds* (*Voet & Rich*, 1970).

σ are given in parentheses.

Bond (Å)	*R*	*U*	*P*
N(1)–C(2)	1·343 (15)	1·332 (22)	1·358 (13)
C(2)–N(3)	1·358 (15)	1·315 (8)	1·309 (4)
N(3)–C(4)	1·344 (13)	1·349 (11)	1·347 (8)
C(4)–C(5)	1·379 (16)	1·365 (14)	1·392 (16)
C(5)–C(6)	1·419 (15)	1·404 (12)	1·424 (33)
N(1)–C(6)	1·336 (12)	1·346 (27)	1·362 (1)
C(5)–N(7)	1·396 (12)	1·388 (18)	1·384 (14)
N(7)–C(8)	1·313 (16)	1·297 (21)	1·320 (11)
C(8)–N(9)	1·358 (14)	1·365 (16)	1·383 (21)
C(4)–N(9)	1·392 (14)	1·370 (18)	1·366 (16)
C(6)–N(6)	1·364 (14)	1·341 (23)	1·315 (5)
Angles (°)	*R*	*U*	*P*
C(6)–N(1)–C(2)	119·9 (0·9)	118·6 (1·4)	123·0 (0·4)
N(1)–C(2)–N(3)	126·8 (0·8)	129·1 (1·5)	125·8 (0·1)
C(2)–N(3)–C(4)	111·1 (1·0)	111·0 (1·0)	111·9 (0·5)
N(3)–C(4)–C(5)	128·0 (1·1)	127·0 (0·4)	127·8 (0·9)
C(4)–C(5)–C(6)	115·4 (0·8)	117·3 (0·9)	116·9 (1·8)
C(5)–C(6)–N(1)	118·6 (1·0)	117·3 (1·6)	114·2 (0·7)
N(3)–C(4)–N(9)	127·6 (1·1)	127·4 (0·9)	127·3 (0·1)
C(6)–C(5)–N(7)	132·0 (1·0)	132·4 (1·1)	131·2 (0·9)
C(5)–N(7)–C(8)	101·8 (0·9)	103·8 (1·2)	104·0 (1·0)
N(7)–C(8)–N(9)	115·7 (0·9)	113·8 (1·4)	112·6 (1·1)
C(8)–N(9)–C(4)	105·6 (1·0)	105·7 (0·7)	106·8 (0·4)
N(9)–C(4)–C(5)	104·5 (0·8)	106·1 (0·7)	104·7 (0·9)
C(4)–C(5)–N(7)	112·4 (1·0)	110·3 (0·8)	111·7 (0·8)
N(1)–C(6)–N(6)	121·4 (0·9)	119·1 (0·7)	120·8 (0·9)
C(5)–C(6)–N(6)	120·0 (0·8)	123·5 (0·7)	124·9 (1·7)

Table 5. *Bond distances* (Å) *and angles* (°) *in the side chain of the title compound, with standard deviations in parentheses*

N(6)—C(10)	1·434 (14)	C(13)–C(17)	1·540 (14)
C(10)–O(11)	1·229 (14)	C(14)–O(15)	1·299 (15)
C(10)–N(12)	1·327 (11)	C(14)–O(16)	1·232 (15)
N(12)–C(13)	1·451 (15)	C(17)–C(18)	1·549 (22)
C(13)–C(14)	1·539 (19)	C(17)–O(19)	1·418 (17)
C(6)—N(6)—C(10)	129·1 (8)	C(14)–C(13)–C(17)	110·5 (10)
N(6)—C(10)–O(11)	117·7 (8)	C(13)–C(14)–O(15)	113·1 (10)
N(6)—C(10)–N(12)	116·6 (10)	C(13)–C(14)–O(16)	122·6 (11)
O(11)–C(10)–N(12)	125·7 (10)	O(15)–C(14)–O(16)	124·3 (12)
C(10)–N(12)–C(13)	118·4 (9)	C(13)–C(17)–C(18)	111·1 (11)
N(12)–C(13)–C(14)	112·8 (10)	C(13)–C(17)–O(19)	108·9 (10)
N(12)–C(13)–C(17)	109·7 (10)	C(18)–C(17)–O(19)	110·6 (11)

Results

The final atomic coordinates and temperature parameters are given in Tables 1 and 2 (see Fig. 1 for the numbering of the atoms). The thermal parameters of the non-hydrogen atoms are shown in Fig. 1.

The least-squares planes of the adenine ring and certain side-chain atoms are given in Table 3. The bond lengths and angles are shown in Tables 4 and 5. The arrangements of molecules in the crystal and the hydrogen-bonding scheme are shown in Figs. 2 and 3.

Discussion

The molecular geometry

The molecules occur in the N(9)–H tautomeric form which appears to be determined by two factors: hydrogen bonding between N(9)–H of the purine ring and O(16) of the ionized carboxyl group (2·751 Å) and coordination of N(7) of purine to Rb (2·899 Å). This

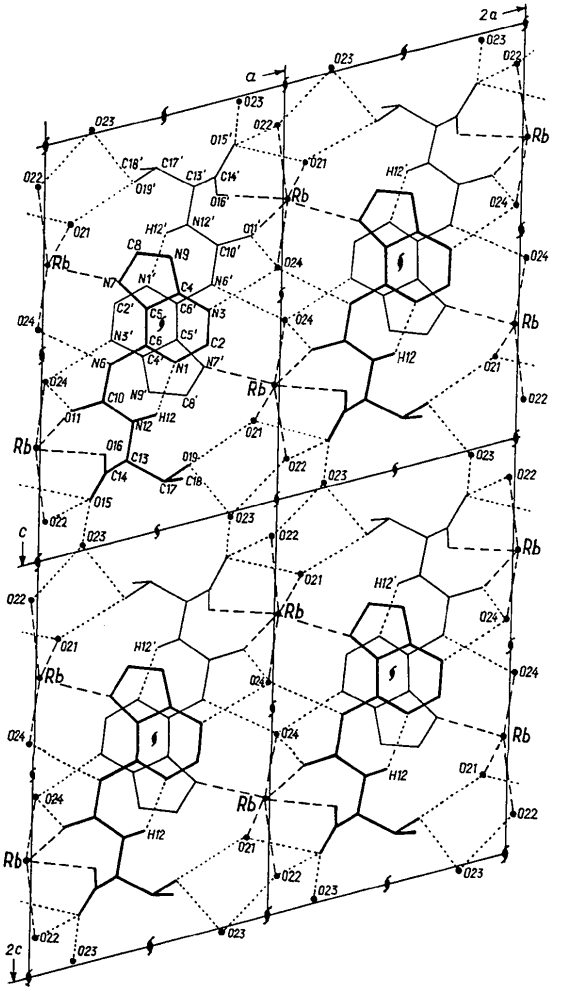

Fig. 2. Projection of the structure along **b**. The dotted lines represent hydrogen bonds, the dashed lines represent coordination round Rb.

tautomer was also found in other N^6-modified adenines, *e.g.* N^6-(Δ^2-isopentenyl)-2-methylthioadenine (McMullan & Sundaralingam, 1971). N^6-(Δ^2-isopentenyl)-adenine (Bugg & Thewalt, 1972), N^6-methyladenine (Sternglanz & Bugg, 1973) and the K salt of *N*-(purin-6-ylcarbamoyl)-glycine monohydrate (Parthasarathy *et al.*, 1974).

The molecular geometry of the Rb salt of *N*-(purin-6-ylcarbamoyl)-L-threonine.$4H_2O$ is characterized by the intramolecular hydrogen bond N(12)-H···N(1). The N(12)–N(1) distance is only 2·693 Å. Parthasarathy *et al.* (1974) have observed the same type of intramolecular hydrogen bond (2·738 Å) in the K salt of *N*-(purin-6-ylcarbamoyl)-glycine monohydrate. The presence of an intramolecular interaction in the molecule appears to define the conformation around the C(6)–N(6) bond which is such that the side chain points away from the imidazole ring. The existence of the intramolecular hydrogen bond leads to two structural consequences: the side chain [the atoms of the ureido system and C(13) and C(17) of threonine] is nearly coplanar with the purine ring; the N(1) site is shielded from involvement in intermolecular hydrogen bonding (see below). As this hydrogen bonding probably occurs in solution (n.m.r. data: Schweizer, Chheda, Baczynskyj & Hall, 1969) it may be important in anticodon loop conformation and may lead to a revision of current views on the structure of cytokinine ureidopurines (Dyson, Hall, Hong, Dutta & Chheda, 1972).

There is a possibility that the hydrogen bond is bifurcated as the distance O(19)–N(12) is 2·783 Å.

The purine moiety is planar within experimental error (Table 3). N(6) is displaced 0·105 Å from the plane. The plane defined by N(6), C(10), O(11), N(12), C(13) and C(17) forms an angle of 1·99° with the plane of the purine ring. The carboxyl and methyl groups of the threonine part are on opposite sides of the plane.

The bond distances and angles in the adenine moiety are different from the values found in the average unprotonated an N(1)-protonated adenine (Voet & Rich, 1970; Saenger, 1971) because N(1) is partially protonated by the intramolecular hydrogen bond and N(7) is coordinated to Rb. As shown in Table 5, significant differences are observed in the distances C(2)–N(3), N(1)–C(6) and C(8)–N(9) and the angles C(6)–N(1)–C(2), N(1)–C(2)–N(3), C(4)–C(5)–C(6), C(5)–C(6)–N(1), C(5)–N(7)–C(8), N(7)–C(8)–N(9), C(5)–C(6)–N(6).

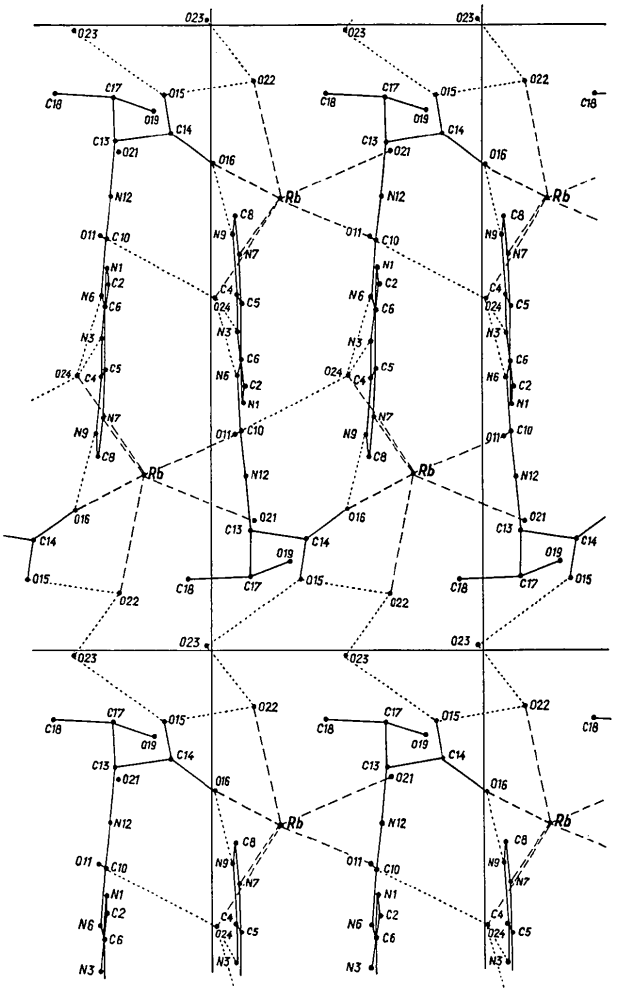

Fig. 3. Packing of molecules in the crystal viewed along a*.

Table 6. *Distances and angles for possible hydrogen-bonded contacts*

A–H···*B*	*A*–*B* (Å)	*A*–H–*B* (°)
N(12)–H···N(1)	2·693 (13)	119
N(9′)—H···O(16)	2·751 (13)	163
O(24)–H···N(3′)	2·879 (13)	
N(6′)—H···O(24)	2·925 (10)	164
O(24)–H···O(11)	3·026 (12)	
N(12)–H···O(19)	2·783 (11)	109
O(21)–H···O(15)	2·954 (13)	
O(22)–H···O(15)	2·701 (14)	
O(23)–H···O(15)	2·768 (13)	
O(21)–H···O(19)	3·001 (15)	
O(19)–H···O(23)	2·737 (11)	
O(22′)–H···O(23)	2·886 (14)	
O(22)–H···O(23)	2·761 (13)	

The molecular packing and intermolecular hydrogen bonding

All the H atoms bonded to the N and O atoms contribute to hydrogen bonding; there is one short intramolecular bond and a number of intermolecular bonds as can be seen in Table 6 and Figs. 2 and 3.

The presence of the intramolecular hydrogen bond N(12)–H···N(1) excludes N(1) from involvement in intermolecular hydrogen bonding. The same shielding of N(1) was observed by Parthasarathy *et al.* (1974) for the K salt of *N*-(purin-6-ylcarbamoyl)glycine monohydrate. A similar situation occurs in the structures of N^6-(Δ^2-isopentenyl)adenines (McMullan & Sundaralingam, 1971; Bugg & Thewalt, 1972) in which close non-bonding contacts of the isopentenyl group shields N(1) from intermolecular hydrogen bonding.

A linking of adenine bases through hydrogen-bond pairs N(6)–H···N(7) and N(9)–H···N(3), which is typical for the purine rings (Voet & Rich, 1970) including the N^6-monoalkylated adenines mentioned above, does not occur in the structure reported here.

Two bases of neighbouring cells are bridged by the H_2O molecule O(24) which is hydrogen-bonded to N(6) and N(3). The H_2O molecules O(24) are hydrogen-bonded also to the O atoms of the ureido system and form a hydrophilic zone about $x=0$ and $z=\frac{1}{2}$ (Figs. 2 and 3). The other three H_2O molecules [O(21), O(22), O(23)] are hydrogen-bonded to hydroxyl and carboxyl groups of the threonine fragments and form a spacious hydrophilic zone about $x=0$ and $z=0$, as shown in Figs. 2 and 3. In this zone the pairs of twofold-screw related H_2O molecules [O(22), O(23)] are hydrogen-bonded to one another and to the O atoms of carboxyl groups to form a twofold helix parallel to **b**.

The purine and threonine fragments of two stacked molecules are joined by the N(9)–H···O(16)-carboxyl hydrogen bond (2·751 Å). The purine rings are stacked in a head-to-tail fashion with an interplanar spacing of about 3·2 Å (Figs. 2 and 3). This type of stacking is in contrast to that observed for N^6-monoalkylated adenines (McMullan & Sundaralingam, 1971; Bugg & Thewalt, 1972; Sternglanz & Bugg, 1973) but is similar to the the glycine analogue (Parthasarathy *et al.*, 1974).

As shown in Fig. 2 Rb is coordinated to six atoms: N(7), O(11)ureido-system, O(16)-carboxyl and O(21), O(22) and O(23) of H_2O molecules. The distances between the Rb and these atoms are given in Table 7.

Table 7. *Bond distances* (Å) *and angles* (°) *around* Rb

Rb–N(7′)	2·899 (9)	O(11)–Rb–O(16)	98·62
Rb–O(11)	2·870 (9)	O(11)–Rb–O(21)	68·98
Rb–O(16)	2·867 (8)	O(11)–Rb–O(22)	125·24
Rb–O(21)	3·103 (12)	O(11)–Rb–O(24)	91·44
Rb–O(22)	2·910 (10)	O(16)–Rb–O(21)	132·23
Rb–O(24)	2·905 (8)	O(16)–Rb–O(22)	75·58
N(7′)–Rb–O(11)	121·34	O(16)–Rb–O(24)	74·63
N(7′)–Rb–O(16)	126·06	O(21)–Rb–O(22)	75·84
N(7′)–Rb–O(21)	97·37	O(21)–Rb–O(24)	147·40
N(7′)–Rb–O(22)	103·31	O(22)–Rb–O(24)	135·51
N(7′)–Rb–O(24)	70·10		

In conclusion, the two sites, N(6)–H and N(1) of the molecule that are normally utilized by adenine bases for complementary pairing in double helical regions of nucleic acids are blocked, owing to the *trans* conformation of the N^6 side chain with respect to the imidazole ring. Watson–Crick pairs are excluded by the presence of the intramolecular hydrogen bond N(12)–H···N(1). This blocking of N(6)–H and N(1) sites suggests that the *N*-(purin-6-ylcarbamoyl)-L-threonine takes part in maintaining the anticodon loop in the single-stranded conformation that enhances codon–anticodon interactions (Fuller & Hodgson, 1967; Kim *et al.*, 1974; Roberts *et al.*, 1974).

A study of *N*-[9-(β-D-ribofuranosyl)purin-6-ylcarbamoyl]-L-threonine by direct methods is also underway and should shed further light on the function of the nucleoside in the structure of tRNA.

We thank Dr R. W. Adamiak, Institute of Organic Chemistry of the Polish Academy of Sciences, for providing the crystals and for helpful discussions. One of us (D.A.A.) thanks Professor M. Wiewiorowki of the same institute for his continuing interest and encouragement. This work was supported by the Polish Academy of Sciences (3.2.01.) and by the Science Research Council, U.K. (P40).

We thank the British Council and the Royal Society for travel and subsistence grants which made this collaboration between our laboratories possible.

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